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Synthesis, Crystal and Molecular Structure, and Spectroscopic Properties of Tris(2,2′-bipyridyl)iron(II) Nitroprusside Tetrahydrate, $[Fe(bpy)_3][Fe(CN)_5NO]\cdot 4H_2O$[1a]

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We have isolated tris(2,2′-bipyridyl)iron(II) nitroprusside by the thermal decomposition of bis(2,2′-bipyridinium) nitroprusside dihydrate at 185 °C in an inert atmosphere. The product readily absorbs atmospheric water and turns into a tetrahydrate that can be also obtained by direct reaction between the component ions in water or by boiling under reflux a solution of nitroprusside and 2,2′-bipyridyl in diluted acetic acid. $[Fe(bpy)_3][Fe(CN)_5NO]\cdot 4H_2O$ crystallizes in the monoclinic system, space group $P2_1/c$, $a = 11.067$ (4) Å, $b = 14.576$ (9) Å, $c = 23.076$ (6) Å, $\beta = 90.91$ (2)°, and $Z = 4$. The molecular structure of the cation is reported for the first time. Infrared, electronic, and Mössbauer spectra are in accordance with the structural results.

Introduction

Our current interest in the properties of cyanometalates prompted us to prepare the supposedly trans and cis isomers of tricyano(2,2′-bipyridyl)nitrosyliron(II) reported by Sarkar et al., as the respective products of the thermal decomposition of bis(2,2′-bipyridinium) nitroprusside dihydrate in an inert atmosphere at 185 °C and of the reaction between nitroprusside and 2,2′-bipyridyl in boiling, diluted acetic acid.[2] Our main interest was the confirmation of the proposed molecular structures by X-ray diffraction techniques. We have been unable to reproduce the reported results and obtain instead the new salt tris(2,2′-bipyridyl)iron(II) nitroprusside tetrahydrate.

The identity of this substance was ascertained by a single-crystal diffraction study. Results were confirmed with crystals obtained by interdiffusion of water solutions of the component ions. An unexpected bonus of this work was the elucidation of the not yet reported molecular structure of the tris(2,2′-bipyridyl)iron(II) cation. As this species is of potential interest as a redox indicator,[3] the study of its properties is also of interest.[4]

Experimental Section

Preparation. Bis(2,2′-bipyridinium) nitroprusside dihydrate $(bpyH)_2[Fe(CN)_5NO]\cdot 2H_2O$ was prepared by double decomposition between stoichiometric amounts of silver nitroprusside and 2,2′-bipyridinium chloride dissolved in water. The mixture was stirred vigorously for 2 h. Silver chloride was separated by filtration, and the solution was concentrated under reduced pressure at room temperature in a rotating evaporator until crystals were obtained. These were separated by filtration, washed with cold water, and vacuum dried over $CaCl_2$. The yield was 70% of the theoretical value.

Tris(2,2′-bipyridyl)iron(II) nitroprusside tetrahydrate was obtained as a product from three independent reactions: (a) by the thermal decomposition at 185 °C for 2 h of $(bpyH)_2[Fe(CN)_5NO]\cdot 2H_2O$ in an electrically heated tube furnace flushed with pure N_2 or CO_2 (the deep violet powdery anhydrous reaction product absorbs water from the atmosphere and turns into the tetrahydrate); (b) by heating for 10 h under reflux a solution of sodium nitroprusside dihydrate and 2,2′-bipyridyl in diluted acetic acid (a method that gives a very low yield); and (c) by direct precipitation when stoichiometric amounts of sodium nitroprusside and tris(2,2′-bipyridyl)iron(II) sulfate solutions were mixed (the tris(2,2′-bipyridyl)iron(II) sulfate was prepared by a well-known method[5]). The sparingly soluble, deep violet product obtained from the solutions was filtered, washed with water, and vacuum dried over $CaCl_2$. Single crystals adequate for an X-ray diffraction study were obtained either by slow spontaneous evaporation of the substance or by interdiffusion of solutions of the component ions. Results of this study pointed to the formula $[Fe(bpy)_3][Fe(CN)_5NO]\cdot 4H_2O$, which was confirmed by the analytical results.

Chemical Analysis. Iron was determined spectrophotometrically in the visible as $[Fe(o\text{-phen})_3]^{2+}$ after dissolution in a mixture of sulfuric, nitric, and hydrochloric acids, dilution with water, and addition of sodium acetate until pH 6 was reached, followed by the successive addition of hydroxylamine hydrochloride and *o*-phenanthroline.[6,7] A reference curve was obtained with Mohr's salt.

C, N, and H were determined by combustion at the Faculty of Biochemistry and Pharmacy of the University of Buenos Aires, República Argentina.

Water of hydration was determined gravimetrically after drying over P_4O_{10} at 100 °C under reduced pressure.

Anal. Calcd for $(bpyH)_2[Fe(CN)_5NO]\cdot 2H_2O$ ($C_{25}FeH_{22}N_{10}O_3$): C, 53.02; Fe, 9.86; H, 3.92; N, 24.73; H_2O, 6.36. Found: C, 54.24; Fe, 9.74; H, 4.12; N, 24.25; H_2O, 6.30.

Anal. Calcd for $[Fe(bpy)_3][Fe(CN)_5NO]\cdot 4H_2O$ ($C_{35}Fe_2H_{32}N_{12}O_5$): C, 51.74; Fe, 13.75; H, 3.97; N, 20.69; H_2O, 8.87. Found for the hydrated pyrolysis product (average of three determinations): C, 53.34; Fe, 14.18; H, 4.02; N, 20.26; H_2O, 8.63.

Density. Crystal density was measured both by flotation in xylene–carbon tetrachloride mixtures and by displacement of benzene in a picnometer thermostated at 25 °C.

Spectra. The IR spectra were recorded with a Perkin-Elmer 457 spectrophotometer both in KBr disks and as Nujol mulls between KBr plates.

Transmission and reflectance UV–visible spectra of aqueous solutions and of solid samples diluted with $BaSO_4$, respectively, were obtained with a Bausch and Lomb Spectronic 600E spectrophotometer.

Mössbauer spectra were provided by Dr. R. Mercader of the Physical Department, Facultad de Ciencias Exactas, Universidad Nacional de La Plata. The spectra were run in a MWE-250 spectrometer with 521 channels using a source of 10 mCi of ^{57}Co in a Rh matrix and calibrated with a natural iron foil of 0.127-mm thickness. The lines were fitted to Lorentzian shape by a nonlinear

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(1) (a) This work was presented as a brief summary at the XXIInd International Conference on Coordination Chemistry, Budapest, Hungary, Aug 23–27, 1982, and as a full communication at the XVIth, Argentine Chemical Congress, Córdoba, República Argentina, Sep 19–24, 1982, and also at the 4th Regional Meeting of the Brazilian Chemical Society, São Carlos, Brazil Nov 8–11, 1982. (b) Supported by fellowships from CICPBA, República Argentina. (c) On leave of absence from the Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, República Argentina. (d) Member of the "Carrera del Investigador Científico", CONICET, República Argentina.

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least-squares program with constraints.

X-ray Diffraction Data. An Enraf-Nonius CAD-4 diffractometer was used with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) to get the necessary information from a prismatic crystal of approximate dimensions 0.2 × 0.2 × 0.25 mm obtained from slow evaporation of an aqueous solution of the thermolysis product. The 25 centered reflections, from least-squares refinement, produced the unit cell dimensions and the orientation matrix for data collection. The 4317 reflections in the ±h, $+k$, $+l$ reciprocal space quadrant having θ in the range 0–25° were measured by the ω–2θ scan technique, using a variable scan speed selected between 2.85 and 20°/min. Intensities of two standard reflections were essentially constant throughout the measurement.

The 2228 independent reflections having $I > 3\sigma(I)$ were used in the calculations. Data were corrected for Lorentz and polarization effects but not for absorption or extinction. The atomic dispersion scattering factors of Cromer and Waber[8] and the anomalous dispersion correction coefficients of Cromer and Ibers[9] were employed in the calculations. Most of these were performed on a VAX computer with the SHELX program.[10] The projection shown below was drawn with the program ORTEP,[11] incorporated in the Enraf-Nonius Structure Determination Package.

Results and Discussion

Stoichiometry. The direct reaction between component ions in aqueous solutions can be represented by

$$[Fe(bpy)_3]^{2+} + [Fe(CN)_5NO]^{2-} \xrightarrow{aq} [Fe(bpy)_3][Fe(CN)_5NO]\cdot 4H_2O$$

while weight changes produced in the thermal decomposition of bis(2,2′-bipyridinium) nitroprusside dihydrate pointed to

$$2(bpyH)_2[Fe(CN)_5NO]\cdot 2H_2O \xrightarrow{185\ ^\circ C} [Fe(bpy)_3][Fe(CN)_5NO] + bpy + NO + 4HCN + {}^1/_2(CN)_2 + 4H_2O$$

The weight loss expected from this reaction is 34.6%, and the obtained value (average of 12 experiments) was 33.1% in good agreement with the calculated value. The presence of NO, HCN, and $(CN)_2$ in the gaseous products of reaction was confirmed by IR spectroscopy by collecting these products in a trap cooled with liquid air and expanding them into an IR absorption cell. If the reaction would have taken the path suggested by Sarkar et al.,[2] neither NO nor $(CN)_2$ should have been found among the gaseous products:

$$(bpyH)_2[Fe(CN)_5NO]\cdot 2H_2O \xrightarrow{185\ ^\circ C} [Fe(CN)_3(bpy)NO] + bpy + 2HCN + 2H_2O$$

In addition, the weight change should have been 43.5%, a value that compares unfavorably with the weight loss found (see above).

Crystal Structure. The crystals are monoclinic, space group $P2_1/c$, with a = 11.067 (4) Å, b = 14.576 (9) Å, c = 23.076 (6) Å, β = 90.91 (2)°, V = 3722 (2) Å^3, Z = 4, D_{calcd} = 1.45 g/cm^3, D_{measd} = 1.44 ± 0.02 g/cm^3, μ(Mo Kα) = 7.67 mm^{-1}, $F(000)$ = 1280 (electrons).

Crystals obtained either by interdiffusion of the component ions or by crystallization of the thermal reaction product (see above) gave the same diffraction patterns.

The iron atoms were readily located from a Patterson map. All other heavy atoms (not hydrogen) were subsequently found by performing a difference Fourier synthesis. Isotropic least squares with unit weights converged to an R factor of 7.6%. Inclusion of hydrogen atoms on stereochemical grounds and the anisotropic refinement of data using the weighting scheme $w = (\sigma^2(F_o) + 0.00076F_o^2)$ gave final R and R_w factors equal to 4.5% and 4.6%, respectively, and the largest parameter shift less than 0.01 of its standard deviation. The minimization function was $M = \sum w(|F_o| - |F_c|)^2$. A fixed vibrational U value of 0.04 Å^2 was assigned to the hydrogen atoms. A final difference map was essentially flat. Final positional parameters and equivalent isotropic temperature factors calculated according to Hamilton[12] are given in Table I. Lists of structure factors, hydrogen atom parameters, and anisotropic thermal parameters are available as supplementary material.

Table I. Final Positional Coordinates and Equivalent Isotropic Thermal Parameters[10] with Standard Deviations in Parentheses

atom	x/a	y/b	z/c	B_{eq}, Å^2
Fe(1)	0.9508 (1)	0.3559 (1)	0.4149 (1)	2.97 (4)
N	0.9162 (6)	0.3547 (5)	0.4842 (3)	4.0 (3)
O	0.8820 (7)	0.3577 (5)	0.5304 (3)	7.4 (3)
C(1)	0.7839 (8)	0.3327 (5)	0.3924 (3)	3.3 (3)
N(1)	0.6840 (6)	0.3188 (5)	0.3834 (3)	5.2 (3)
C(2)	0.9281 (7)	0.4870 (6)	0.4067 (3)	3.4 (3)
N(2)	0.9155 (6)	0.5650 (5)	0.4020 (3)	4.7 (3)
C(3)	1.1248 (8)	0.3723 (5)	0.4271 (3)	3.3 (3)
N(3)	1.2271 (6)	0.3804 (5)	0.4324 (3)	4.5 (3)
C(4)	0.9826 (7)	0.2262 (6)	0.4060 (3)	3.4 (3)
N(4)	0.9999 (7)	0.1492 (5)	0.3993 (3)	4.9 (3)
C(5)	0.9811 (7)	0.3626 (5)	0.3333 (4)	3.0 (3)
N(5)	1.0005 (6)	0.3669 (4)	0.2840 (3)	3.6 (3)
O(W1)	0.4764 (5)	0.2107 (5)	−0.0461 (2)	6.4 (3)
O(W2)	0.4063 (7)	0.1007 (6)	0.4677 (3)	9.6 (4)
O(W3)	0.1693 (7)	0.3574 (6)	0.0189 (4)	10.6 (4)
O(W4)	0.0991 (8)	0.2558 (5)	0.1191 (4)	11.5 (5)
Fe(2)	0.5796 (1)	0.3048 (1)	0.1719 (0)	2.54 (4)
N(11)	0.4806 (5)	0.2703 (4)	0.2382 (3)	2.9 (2)
C(11)	0.5066 (7)	0.2085 (6)	0.2800 (3)	3.6 (3)
C(12)	0.4300 (9)	0.1862 (6)	0.3240 (4)	4.1 (3)
C(13)	0.3237 (9)	0.2299 (7)	0.3269 (4)	4.9 (4)
C(14)	0.2908 (7)	0.2919 (7)	0.2860 (4)	4.6 (4)
C(15)	0.3732 (7)	0.3125 (6)	0.2411 (3)	3.6 (3)
N(12)	0.4428 (6)	0.3862 (4)	0.1562 (3)	3.1 (2)
C(16)	0.3521 (7)	0.3798 (5)	0.1945 (4)	3.3 (3)
C(17)	0.2482 (8)	0.4338 (7)	0.1903 (4)	5.1 (4)
C(18)	0.239 (1)	0.4973 (7)	0.1457 (5)	6.6 (5)
C(19)	0.336 (1)	0.5059 (7)	0.1081 (4)	5.9 (4)
C(110)	0.4346 (8)	0.4492 (6)	0.1140 (4)	4.2 (3)
N(21)	0.5146 (5)	0.2001 (4)	0.1291 (2)	2.4 (2)
C(21)	0.4094 (7)	0.1963 (6)	0.0992 (3)	3.2 (3)
C(22)	0.3723 (7)	0.1186 (7)	0.0686 (3)	3.6 (3)
C(23)	0.4473 (9)	0.0420 (6)	0.0693 (4)	4.5 (4)
C(24)	0 5537 (8)	0.0454 (5)	0.0994 (3)	3.6 (3)
C(25)	0.5852 (7)	0.1254 (5)	0.1285 (3)	2.6 (3)
N(22)	0.7067 (5)	0.2165 (4)	0.1899 (2)	2.5 (2)
C(26)	0.6966 (7)	0.1336 (5)	0.1638 (3)	2.4 (3)
C(27)	0.7835 (8)	0.0658 (5)	0.1708 (3)	3.8 (3)
C(28)	0.8816 (8)	0.0813 (6)	0.2067 (4)	4.0 (3)
C(29)	0.8923 (7)	0.1641 (6)	0.2354 (4)	3.9 (3)
C(210)	0.8017 (7)	0.2302 (5)	0.2261 (3)	3.2 (3)
N(31)	0.6619 (5)	0.4075 (4)	0.2110 (3)	2.6 (2)
C(31)	0.6421 (7)	0.4390 (5)	0.2652 (3)	3.3 (3)
C(32)	0.7070 (8)	0.5114 (6)	0.2887 (3)	3.6 (3)
C(33)	0.7917 (8)	0.5555 (5)	0.2558 (4)	3.4 (3)
C(34)	0.8128 (7)	0.5252 (5)	0.2002 (3)	3.4 (3)
C(35)	0.7455 (7)	0.4521 (5)	0.1796 (3)	2.9 (3)
N(32)	0.6772 (5)	0.3473 (4)	0.1068 (2)	2.6 (2)
C(36)	0.7563 (7)	0.4153 (5)	0.1197 (3)	2.7 (3)
C(37)	0.8408 (7)	0.4471 (5)	0.0801 (4)	3.6 (3)
C(38)	0.8407 (8)	0.4096 (6)	0.0250 (4)	4.1 (3)
C(39)	0.7570 (7)	0.3423 (6)	0.0113 (3)	3.5 (3)
C(310)	0.6777 (7)	0.3133 (5)	0.0531 (3)	3.0 (3)

A left ORTEP projection of the content of one asymmetric unit down the unique axis displaying the conformational

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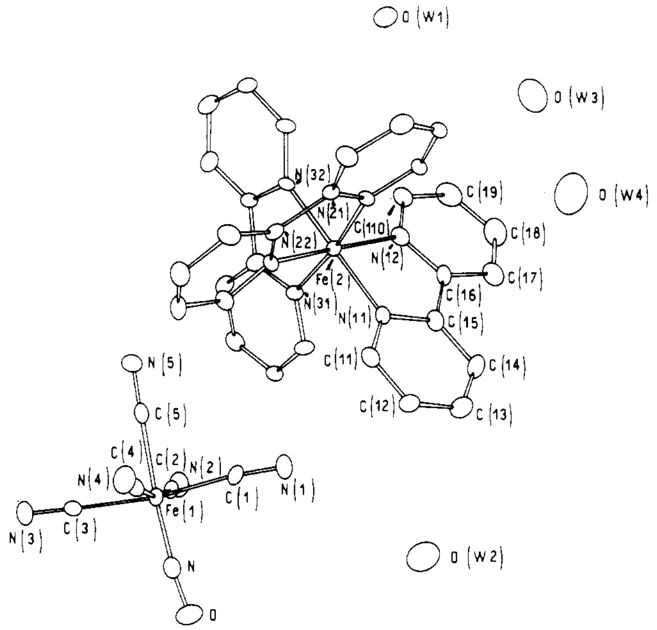

Figure 1. Projection along *b* of the asymmetric unit of tris(2,2′-bipyridyl)iron(II) nitroprusside tetrahydrate ([Fe(bpy)$_3$][Fe(CN)$_5$NO]·4H$_2$O). For the sake of clarity, the complete atom numbering of only one 2,2′-bipyridyl ligand is shown: N(11), N(12), and C(11) through C(110).

Table II. Bond Distances (Å) in the Nitroprusside Anion and in the Tris(2,2′-bipyridyl)iron(II) Cation and Water Oxygen Short Contacts (Å)

	(a) Nitroprusside		
Fe(1)-N	1.650 (7)	N-O	1.14 (1)
Fe(1)-C(1)	1.940 (8)	C(1)-N(1)	1.14 (1)
Fe(1)-C(2)	1.936 (9)	C(2)-N(2)	1.15 (1)
Fe(1)-C(3)	1.956 (8)	C(3)-N(3)	1.14 (1)
Fe(1)-C(4)	1.935 (9)	C(4)-N(4)	1.15 (1)
Fe(1)-C(5)	1.920 (9)	C(5)-N(5)	1.16 (1)
	(b) Tris(2,2′-bipyridyl)iron(II)		
Fe(2)-N(11)	1.961 (6)	C(24)-C(25)	1.39 (1)
Fe(2)-N(12)	1.953 (6)	C(25)-N(21)	1.340 (9)
Fe(2)-N(21)	1.949 (6)	N(22)-C(26)	1.354 (9)
Fe(2)-N(22)	1.947 (6)	C(26)-C(27)	1.39 (1)
Fe(2)-N(31)	1.964 (6)	C(27)-C(28)	1.37 (1)
Fe(2)-N(32)	1.964 (6)	C(28)-C(29)	1.38 (1)
N(11)-C(11)	1.35 (1)	C(29)-C(210)	1.41 (1)
C(11)-C(12)	1.37 (1)	C(210)-N(22)	1.347 (9)
C(12)-C(13)	1.34 (1)	C(25)-C(26)	1.47 (1)
C(13)-C(14)	1.35 (1)	N(31)-C(31)	1.353 (9)
C(14)-C(15)	1.42 (1)	C(31)-C(32)	1.38 (1)
C(15)-N(11)	1.34 (1)	C(32)-C(33)	1.38 (1)
N(12)-C(16)	1.35 (1)	C(33)-C(34)	1.38 (1)
C(16)-C(17)	1.40 (1)	C(34)-C(35)	1.38 (1)
C(17)-C(18)	1.39 (2)	C(35)-N(31)	1.351 (9)
C(18)-C(19)	1.40 (2)	N(32)-C(36)	1.352 (9)
C(19)-C(110)	1.37 (1)	C(36)-C(37)	1.40 (1)
C(110)-N(12)	1.34 (1)	C(37)-C(38)	1.38 (1)
C(15)-C(16)	1.47 (1)	C(38)-C(39)	1.38 (1)
N(21)-C(21)	1.345 (9)	C(39)-C(310)	1.38 (1)
C(21)-C(22)	1.39 (1)	C(310)-N(32)	1.335 (9)
C(22)-C(23)	1.39 (1)	C(35)-C(36)	1.49 (1)
C(23)-C(24)	1.36 (1)		
	(c) Water Oxygen Short Contacts[a]		
O(W1^{i})-N(1^{ii})	2.87 (2)	O(W3^{i})-O(W4^{i})	2.86 (2)
O(W1^{i})-O(W2^{ii})	2.88 (2)	O(W4^{i})-N(2^{iii})	2.83 (2)
O(W2^{ii})-O(W3^{i})	2.96 (2)		

[a] Symmetry code: (i) x, y, z; (ii) $x, \bar{y} + {}^1/_2, z - {}^1/_2$; (iii) $\bar{x} + 1, y - 1, \bar{z}$.

Table III. Bond Angles (deg) in the Nitroprusside Anion and in the Tris(2,2′-bipyridyl)iron(II) Cation

	(a) Nitroprusside		
N-Fe(1)-C(1)	91.3 (3)	C(2)-Fe(1)-C(5)	83.0 (3)
N-Fe(1)-C(2)	94.2 (3)	C(3)-Fe(1)-C(4)	87.4 (3)
N-Fe(1)-C(3)	96.0 (3)	C(3)-Fe(1)-C(5)	87.0 (3)
N-Fe(1)-C(4)	97.9 (3)	C(4)-Fe(1)-C(5)	84.9 (3)
N-Fe(1)-C(5)	175.9 (3)	Fe(1)-N-O	173.4 (7)
C(1)-Fe(1)-C(2)	91.4 (3)	Fe(1)-C(1)-N(1)	175.0 (7)
C(1)-Fe(1)-C(3)	172.1 (3)	Fe(1)-C(2)-N(2)	179.5 (6)
C(1)-Fe(1)-C(4)	88.6 (3)	Fe(1)-C(3)-N(3)	177.6 (7)
C(1)-Fe(1)-C(5)	85.8 (3)	Fe(1)-C(4)-N(4)	178.2 (7)
C(2)-Fe(1)-C(3)	91.1 (3)	Fe(1)-C(5)-N(5)	179.4 (7)
C(2)-Fe(1)-C(4)	167.9 (3)		
	(b) Tris(2,2′-bipyridyl)iron(II)		
N(11)-Fe(2)-N(12)	81.9 (3)	N(12)-Fe(2)-N(32)	95.8 (2)
N(11)-Fe(2)-N(21)	89.3 (2)	N(21)-Fe(2)-N(22)	81.3 (2)
N(11)-Fe(2)-N(22)	94.3 (2)	N(21)-Fe(2)-N(31)	173.7 (2)
N(11)-Fe(2)-N(31)	95.7 (2)	N(21)-Fe(2)-N(32)	93.5 (2)
N(11)-Fe(2)-N(32)	176.5 (3)	N(22)-Fe(2)-N(31)	94.5 (2)
N(12)-Fe(2)-N(21)	95.9 (2)	N(22)-Fe(2)-N(32)	88.1 (2)
N(12)-Fe(2)-N(22)	175.4 (3)	N(31)-Fe(2)-N(32)	81.6 (2)
N(12)-Fe(2)-N(31)	88.6 (2)		

	$i = 1$	$i = 2$	$i = 3$
Fe(2)-N(*i*1)-C(*i*1)	127.9 (5)	127.0 (5)	127.0 (5)
Fe(2)-N(*i*1)-C(*i*5)	115.3 (5)	115.5 (4)	115.9 (5)
C(*i*5)-N(*i*1)-C(*i*1)	116.8 (7)	117.5 (6)	117.1 (6)
N(*i*1)-C(*i*1)-C(*i*2)	124.1 (7)	122.6 (7)	122.1 (7)
C(*i*1)-C(*i*2)-C(*i*3)	118.5 (8)	118.4 (7)	119.7 (7)
C(*i*2)-C(*i*3)-C(*i*4)	120.6 (9)	119.3 (8)	119.4 (7)
C(*i*3)-C(*i*4)-C(*i*5)	118.7 (8)	119.2 (8)	118.0 (7)
C(*i*4)-C(*i*5)-C(*i*6)	125.2 (7)	122.6 (7)	123.2 (7)
C(*i*4)-C(*i*5)-N(*i*1)	121.2 (7)	123.1 (7)	123.9 (7)
N(*i*1)-C(*i*5)-C(*i*6)	113.6 (7)	114.3 (6)	113.0 (6)
C(*i*5)-C(*i*6)-C(*i*7)	123.2 (8)	125.5 (7)	123.5 (7)
C(*i*5)-C(*i*6)-N(*i*2)	114.4 (7)	112.4 (6)	114.0 (6)
C(*i*7)-C(*i*6)-N(*i*2)	122.4 (8)	122.1 (6)	122.5 (7)
C(*i*6)-N(*i*2)-Fe(2)	114.7 (5)	116.2 (4)	115.1 (5)
C(*i*6)-N(*i*2)-C(*i*10)	118.7 (7)	117.8 (6)	117.7 (6)
C(*i*10)-N(*i*2)-Fe(2)	126.5 (5)	126.1 (5)	127.1 (5)
N(*i*2)-C(*i*10)-C(*i*9)	121.9 (8)	122.8 (7)	123.2 (7)
C(*i*10)-C(*i*9)-C(*i*8)	120.1 (9)	118.1 (7)	119.3 (7)
C(*i*9)-C(*i*8)-C(*i*7)	118 (1)	119.6 (7)	118.8 (8)
C(*i*8)-C(*i*7)-C(*i*6)	118.6 (9)	119.5 (7)	118.6 (7)

features of the complexes and atom numbering is shown in Figure 1. The nitroprusside anion has the usual umbrella-like distorted-octahedral geometry with a mean angle between the iron atom and the nitrosyl and equatorial cyanide groups of about 95° in agreement with previous determinations.[13] The Fe–N distance (1.650 (7) Å) and the mean Fe–C distance (1.94 (1) Å) are also in close agreement with previous studies.[13]

The six nitrogen atoms in the tris(2,2′-bipyridyl)iron(II) cation form a distorted octahedron around the iron ion with a mean Fe–N distance of 1.956 (8) Å. In comparison, the N–N intraligand distances (mean 2.56 (1) Å) are too short to ensure Fe–ligand angles of 90° (mean found 81.6 (3)°) as required by a perfect octahedron.

The 2,2′-bipyridyl ligands are all planar within the experimental accuracy. There are no significant differences in the structure of bipyridyl groups in [Fe(bpy)$_3$]$^{2+}$ as compared with related complexes;[14] namely, mean bond lengths found for the bipyridyl groups in the iron complex (*d*(C–N) = 1.346 (6) Å, *d*(ring C–C) = 1.38 (2) Å, and *d*(inter-ring C–C) = 1.48 (1) Å) are all in agreement with values reported for the other complexes within experimental error.

The four water molecules in the unit cell form a chain with their oxygen atoms at short contact in the distance range 2.86–2.96 Å. The chain bridges two nitroprusside ions through

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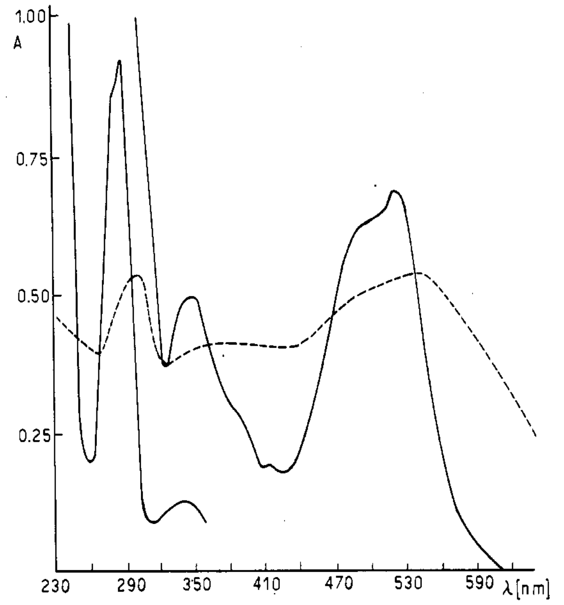

Figure 2. Electronic spectra of $[Fe(bpy)_3][Fe(CN)_5NO]\cdot 4H_2O$ in aqueous solution (—) and as a solid diluted with $BaSO_4$ (- - -).

cyanide nitrogens. The rather high thermal parameters of water oxygens $O(W_2)$, $O(W_3)$, and $O(W_4)$ might be due to positional or occupational disorder.

Bond distances for the anion and the cation and water oxygen short contacts are included in Table II. Bond angles for the complex ions are listed in Table III.

Electronic Spectra. Figure 2 depicts the UV-visible reflectance and transmission spectra of the substance as solid and in aqueous solutions. The similarity of the spectra of samples obtained both by metathesis and by thermal decomposition (after hydration) provides further proof to the identity of both products.

The spectra are dominated by the intense bands of the cation that in the solution spectra show features at 522, 488, 418 (sh), 296, and 290 nm (literature values: 524.9, 490, 415, 298, and 290 nm[15]). Corresponding molar absorptivities measured at 1.97×10^{-4} M concentration in the visible and 1.57×10^{-5} M in the ultraviolet (the systems do not obey strictly the Beer law) were respectively 8100, 7160, 2270, 60 687, and 55 725 $mol^{-1}\ dm^3\ cm^{-1}$. Wavelengths of features seen in the reflectance spectra are 537, 496, 305, and 292 nm. A solvatochromic band shift is clearly observed. This is in agreement with the reddish tinge of the solution (other $[Fe(bpy)_3]^{2+}$ salts are in fact blood red colored). Nitroprusside has only weak bands and shoulders in the spectral region covered by our spectrophotometer, its most intense peak being at 200 nm. Assignments can be found in the literature.[16]

Infrared Spectrum. The spectrum of a sample obtained by metathesis is available as supplementary material. It shows the typical features of hydration water and component ions of the substance. Water bands appear at 3448 cm^{-1} (stretch) and 1635 cm^{-1} (scissor). The broadness of these bands and lack of distinct peaks suggest that all hydrogens are (hydrogen) bonded in correspondence with the short $O_W \cdots O_W$ and $O_W \cdots N$ distances found (see Table II). Nitroprusside bands are seen at 2138 cm^{-1} (CN stretching), 1898 cm^{-1} (NO stretching), 660 cm^{-1} (FeNO angular deformation), 650 cm^{-1} (Fe–N stretching), and 428 and 408 cm^{-1} (FeCN deformation and Fe–C stretching). Interestingly, the wavenumber of the NO stretching is one of the lowest observed in a long series of nitroprussides[17] (the lowest of all are values observed for the nitroprussides of the big organic cations tetraphenylphosphonium and tetraphenylarsonium at 1878 and 1882 cm^{-1}, respectively[18]). In these salts,[19] as in the substance reported hereby, the anions are far isolated from each other while in some alkaline-earth nitroprussides, including $Ba[Fe(CN)_5NO]\cdot 2H_2O$[20,21] and $Sr[Fe(CN)_5NO]\cdot nH_2O$ (n = 2,4)[13,22] where the NO stretching band appears at about 1960 cm^{-1} in the IR spectrum, the anions are interspersed, with the NO groups arranged in nearly eclipsed, antiparallel positions and at a relatively short distance (about 4 Å) from each other. This geometry gives place to an intermolecular vibrational coupling, which affects the position and shape of the strong NO stretching band in the IR spectrum. This subject matter is currently under investigation in this laboratory where $N^{18}O$-enriched samples of $Sr[Fe(CN)_5NO]\cdot 4H_2O$ are under study. At low $N^{18}O$ content, no vibrational coupling is observed, while at increasing $N^{18}O$ concentrations it makes itself evident.[23]

Table IV. Isomeric Shifts and Quadrupolar Splittings Assigned to Tris(2,2′-bipyridyl)iron(II) Nitroprusside Tetrahydrate

ion	isomeric shift,[a] mm/s		quadrupolar splitting, mm/s		ref
	found	lit.	found	lit.	
$[Fe(bpy)_3]^{2+}$	0.29	0.325	0.32	0.39	25
$[Fe(CN)_5NO]^{2-}$	−0.26	−0.26	1.88	1.7037	26

[a] Referred to natural iron.

Bands due to the cation are at 3112, 3080, 3058, 3031, 1606, 1568, 1468, 1445, 1428, 1315, 1274, 1246, 1161, 767, and 734 cm^{-1}, and their assignments can be found in literature.[24]

Spectra of samples of different origins were alike, and only slight differences have been noted in the position of the NO stretching, confirming the high sensitivity of this band to perhaps small physical differences.

Mössbauer Spectra. Again, similar results were obtained with samples from the three preparative methods, Table IV presents the average of these results together with value for the anion and the cation taken from the literature. The agreement is quite satisfactory.

All results seem to confirm therefore that the product of the thermal decomposition of bis(2,2′-bipyridinium) nitroprusside dihydrate as well as the product of the reaction of nitroprusside and 2,2′-bipyridyl in boiling diluted acetic acid is tris(2,2′-bipyridyl)iron(II) nitroprusside instead of tri-

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cyano(2,2'-bipyridyl)nitrosyliron(II) (either trans or cis).

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Registry No. [Fe(bpy)$_3$][Fe(CN)$_5$NO]·4H$_2$O, 88245-17-4; (bpyH)$_2$[Fe(CN)$_5$NO], 88245-16-3; sodium nitroprusside, 14402-89-2.

Supplementary Material Available: IR spectrum of [Fe(bpy)$_3$]-[Fe(CN)$_5$NO]·4H$_2$O in a KBr disk (Figure 3), a stereoscopic ORTEP projection along the crystal unique axis of the asymmetric unit of [Fe(bpy)$_3$][Fe(CN)$_5$NO]·4H$_2$O (Figure 4), listings of anisotropic thermal parameters for all non-hydrogen atoms (Table V), fractional coordinates of the 2,2'-bipyridyl hydrogens (Table VI), and structure factor amplitudes (Table VII) (16 pages). Ordering information is given on any current masthead page.

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Dehalogenation of Binuclear Arene–Ruthenium Complexes: A New Route to Homonuclear Triruthenium and Heteronuclear Ruthenium–Iron Cluster Complexes Containing Chelating Phosphorus Ligands. Crystal Structure of $Ru_3(CO)_{10}(Ph_2PCH_2PPh_2)$

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The binuclear complexes (RuCl$_2$(*p*-cymene))$_2$(Ph$_2$P(CH$_2$)$_n$PPh$_2$) (**2**, $n = 2$; **4**, $n = 1$) obtained from (RuCl$_2$(*p*-cymene))$_2$ have been reacted with an excess of Fe$_2$(CO)$_9$. The former derivative, **2**, yielded FeRu(CO)$_8$(Ph$_2$PCH$_2$CH$_2$PPh$_2$) (**5**), (Fe$_2$Ru(μ-CO)$_2$(CO)$_9$)$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$) (**6**), Ru$_3$(μ-Cl)$_2$(CO)$_8$(Ph$_2$PCH$_2$CH$_2$PPh$_2$) (**7**), and FeRu$_2$(μ-Cl)$_2$(CO)$_8$-(Ph$_2$PCH$_2$CH$_2$PPh$_2$) (**8**) (noticeably, thermolysis of **8** under mild conditions yielded **7**). The latter derivative, **4**, afforded Ru$_3$(CO)$_{10}$(Ph$_2$PCH$_2$PPh$_2$) (**9**) and FeRu$_2$(CO)$_{10}$(Ph$_2$PCH$_2$PPh$_2$) (**10**). The X-ray crystal structure of **9** has been determined: monoclinic crystals, space group $P2_1/c$ with $a = 13.122$ (3) Å, $b = 12.040$ (4) Å, $c = 23.658$ (7) Å, $\beta = 103.44$ (2)°, and $Z = 4$. Final R and R_w values are respectively 0.036 and 0.041 on the basis of 4346 independent reflections. The Ph$_2$PCH$_2$PPh$_2$ group that bridges a Ru–Ru bond occupies equatorial positions. Interatomic distances of interest are Ru(1)–Ru(2) = 2.834 (1), Ru(1)–Ru(3) = 2.841 (1), and Ru(2)–Ru(3) = 2.860 (1) Å. The shortest bond Ru(1)–Ru(2) is supported by the chelating phosphorus ligand (Ru(1)–P(1) = 2.322 (2) and Ru(2)–P(2) = 2.334 (2) Å). Ru–P bonds are not coplanar as shown by the dihedral angle P(1)–Ru(1)–Ru(2)/P(2)–Ru(2)–Ru(1) = 19.1 (1)°. Such a distortion induces a disturbance in the distribution of CO ligands with respect to Ru$_3$(CO)$_{12}$. Of particular interest is the bending of every axial carbonyl toward one Ru–Ru bond.

Introduction

Mixed-transition-metal polymetallic complexes have aroused interest recently as much for the novelty of their structure as for the potential offered by their reactivity.[1,2] Among these, ruthenium–iron complexes have specially attracted attention for the versatility of a broad range of phosphine-containing ruthenium catalysts and for the evidence that addition of iron carbonyls to ruthenium catalysts enhances the activity of the catalyst toward the water-gas shift reaction.[3] Moreover, in order to understand how mixed-metal clusters behave as catalysts, or as catalyst precursors, ruthenium–iron complexes have been recently designed for the elucidation of basic reactivity patterns involving a multisite system.[4,5]

In previous work we have indicated that the readily available mononuclear benzene–ruthenium(II) complexes RuCl$_2$-(PR$_3$)(C$_6$H$_6$)[6] could act as convenient precursors of [RuPR$_3$] fragments to afford FeRu$_2$(μ-Cl)$_2$(CO)$_8$(PR$_3$)$_2$ complexes.[7] In the same way, we have now investigated the reactivity of dinuclear arene–ruthenium(II) complexes (RuCl$_2$(arene))$_2$-(Ph$_2$P(CH$_2$)$_n$PPh$_2$) toward Fe$_2$(CO)$_9$ in order to synthesize mixed-metal complexes. We have found that the dehalogenation reaction depends on the nature of the bridging phosphine group, is either partial (with Ph$_2$PCH$_2$CH$_2$PPh$_2$) or complexes (with Ph$_2$PCH$_2$PPh$_2$), and affords a series of new mixed-metal iron–ruthenium complexes. Although the use of bimetallic precursors supported by bridging ligands could be expected to provide satisfactory control of the number of Ru centers in the resulting species, we also find trinuclear Ru$_3$ complexes among the reaction products. Typically, the formation of Ru$_3$(CO)$_{10}$(Ph$_2$PCH$_2$PPh$_2$) is an unexpected feature, showing the complexity of the reaction pathway.

The X-ray structure of this complex is reported here. The geometric features are discussed in comparison with those of Ru$_3$(CO)$_{12}$[8] and Ru$_3$(CO)$_8$(Ph$_2$PCH$_2$PPh$_2$)$_2$.[9] The solid-state structure of Ru$_3$(CO)$_{10}$(Ph$_2$PCH$_2$PPh$_2$) suggests an alternative mechanism for the previously reported CO-exchange process found for this complex.[10]

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